

Dipole fluid as a basic model for the equation of state of ionic liquid in the vicinity of their critical point

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The model of dipole fluid for the ionic liquids similar to the molten NaCl is proposed. The estimates for the critical parameters are obtained with the help of the van der Waals equation of state. The influence of the rotation on the characteristics of a dipole pair and the location of the critical point is discussed. The dissociation of such fluid near the critical point is considered.

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Introduction

There is the strong indication for existence of the liquid-gas critical point in ionic liquids like molten NaCl. The main model for such systems is called Primitive Model or its restricted version where the characteristics (mass, diameter etc.) of the opposite charges are the same. Because of formation of associated ionic pairs the derivation of mean field equation of state in rigorous thermodynamic approach is yet unsolved. The existence of additional constraints, so called sum rules [1], makes the problem of finding thermodynamically consistent mean field theory hard to solve comparing with the molecular liquid case. The various approaches have been proposed recently for the derivation of equation of state (EOS) for the RPM. Mostly they are based either on the improvements of classical Debye-Hückel (DH) [2] and Bjerrum [3] theory of association or Mean Spherical Approximation (MSA) [4] taking into account the association and various effective interactions. For the reviews of the results see [5, 6, 7, 8, 9].

The location of the critical point for RPM varies in dependence of the interactions included into free energy. It is accepted that the following dimensionless parameters for the temperature T , particle number density n and pressure P are used:

$$T^* = \frac{k_B T}{q^2/a}, \quad \rho^* = n a^3, \quad P^* = \frac{P}{q^2/a^4} \quad (1)$$

where a is the ionic diameter q is the absolute value of the charge. The characteristic value for T_c^* takes the values in the interval $0.05 \leq T_c^* \leq 0.08$. The situation with the critical density ρ_c is less definite. Its value varies from $\rho_c = 0.02$ to $\rho_c = 0.08$. It should be noted that most of the analytical results predict low density ($\rho_c = 0.026$) and "high temperature" ($T_c^* = 0.06 - 0.08$) critical point. It cannot be excluded that such low value for ρ_c^* is connected with small association taken into account with the help of thermodynamic perturbation theory. However the reliability of such type estimates is not quite clear. Therefore the development of the alternative approach grounded on the dipole fluid model seem to be expedient.

The Monte Carlo (MC) simulation studies [10, 11, 12] performed in recent years give "high density" $\rho_c = 0.07 - 0.08$ and low temperature $T_c^* = 0.04 - 0.05$ critical point.

In the present paper we estimate the critical characteristics of the ionic molten in the framework of the dipole fluid approach. We will also show that the change of molecular parameters due to rotations influences essentially the location of the critical point.

I. QUALITATIVE ANALYSIS OF THE CRITICAL BEHAVIOR OF THE DIPOLE LIQUID

NaCl is the simplest example of ionic liquid. In solid state it is ionic crystal. Above the melting point the positions of ions become unfixed, but this liquid remains strongly dissociated. Due to thermal expansion at increasing temperature the dissociation degree diminishes and the molten salt passes to a dipole liquid. At further increasing temperature and decreasing the molten density the dissociation degree grows again and the molten salt becomes completely ionized

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system. Thus, at some temperature (T_1, T_2) and density (n_1, n_2) intervals the molten NaCl can be considered as a dipole liquid. Further the additional arguments for this assumption will be given.

Let us consider the general properties of this liquid and, in particular, its main critical parameters: the critical temperature and density. The interparticle interaction in dipole system takes the form:

$$U(1, 2) = U_w(1, 2) + U_{dd}(1, 2) \quad (2)$$

where the first term describes the Van-der-Waals interaction between molecules and

$$U_{dd} = \frac{1}{\epsilon r_{12}^3} \left(\vec{d}_1 \vec{d}_2 - 3 \frac{(\vec{d}_1 \vec{r}_{12})(\vec{d}_2 \vec{r}_{12})}{r_{12}^2} \right) \quad (3)$$

the proper dipole-dipole interaction, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interparticle spacing. Note that the dipole moment of a pair is some function of the equilibrium distance between ions in a pair:

$$\mathbf{d}_i = d(r_d) \mathbf{n}_i, \quad \mathbf{n}_+ = \frac{\mathbf{r}_+^{(i)} - \mathbf{r}_-^{(i)}}{|\mathbf{r}_+^{(i)} - \mathbf{r}_-^{(i)}|},$$

$i = 1, 2$, ϵ is dielectric permittivity.

Because of the dipole-dipole interactions are relatively weak the angular distribution of dipole moments \vec{d}_i is close to isotropic one. More exactly we assume that the two particle distribution function $g(\vec{d}_1, \vec{d}_2)$ can be approximated by the first two terms in the expansion:

$$g(\vec{d}_1, \vec{d}_2) = 1 - \beta U_{dd}(1, 2) + \dots, \quad \beta = \frac{1}{k_B T}. \quad (4)$$

The approximation of such a kind allows us to exclude the orientational degrees of freedom in the configurational integral with the help of the perturbation theory. In fact this procedure is equivalent to the usage of the isotropic potential

$$U(r_{12}) = \langle U(1, 2) \rangle = U_w(r_{12}) - U_d \left(\frac{\sigma}{r_{12}} \right)^6, \quad (5)$$

$$U_d = \frac{2}{3} \beta \frac{\langle d^2 \rangle^2}{\epsilon^2 \sigma^6}$$

Here $\sigma \approx a_+ + a_- \approx 2a$, a_+ and a_- are the diameters of ions Na and Cl correspondingly and for simplicity we put $a_+ = a_-$ and neglect the difference in masses of the ions, $\langle \dots \rangle$ denotes the average with internal partition function of a pair. It is easy to check that the inequality $|U_w(r_{12})| \ll U_d \left(\frac{\sigma}{r_{12}} \right)^6$ takes place at all r_{12} . Therefore further the contribution $|U_w|$ will be ignored.

It is essential, that the averaging procedure restricts the applicability region of the potential (5) by interparticle spacings $\sigma \leq r_{12}$ which gives the size of the "averaged" dipole of order $2a$. Though the value of σ may be slightly less than $2a$ since rotating dipoles are not the same as hard spheres of diameter $2a$. It is quite clear in view of scattering cross section for the hard rotating dumbbells. At this level σ should be considered as the parameter (in general temperature dependent) of the dipole-dipole potential. The procedure of its fixing in the critical point will be discussed further.

To describe the properties of the molten NaCl within the interval, where it can be considered as a dipole liquid, we can use the potential with hard wall:

$$U(r_{12}) = \begin{cases} \infty & , r_{12} < \sigma \\ -U_d \left(\frac{\sigma}{r_{12}} \right)^6 & , \sigma \leq r_{12} \end{cases} \quad (6)$$

Such a potential leads to the Van-der-Waals equation of state

$$P = \frac{n_d k_B T}{1 - n_d b} - A(T) n_d^2, \quad (7)$$

where

$$A(T) = -\pi \int_{\sigma}^{\infty} U(r, T) r^2 dr = \frac{\pi \sigma^3}{3} U_d, \quad b = \frac{2\pi}{3} \sigma^3 \quad (8)$$

and n_d is the pair number density. Therefore the overall density is $n = 2n_d$. In dimensionless form (7) and (8) read as:

$$P^* = \frac{\rho^* T^*}{2 - b\rho^*} - \frac{\tilde{A}(T^*)}{4} \rho^{*2}, \quad (9)$$

and

$$\tilde{A}(T^*) = \frac{2\pi}{9T^*\sigma^3} \langle\langle r_d^2 \rangle\rangle^2 \quad (10)$$

Here all spatial parameters is given in units of a . The value of parameter $\langle\langle r_d \rangle\rangle$ depends on the internal structure of the pair. Though by the order of magnitude $\langle\langle r_d \rangle\rangle \approx 1$, nevertheless from [13] it follows that the characteristic values of dipole moments correspond to $\langle\langle r_d \rangle\rangle < 1$.

Since σ is connected with the size of the pair we model its temperature dependence via relation:

$$\sigma = \langle\langle r_d \rangle\rangle \delta \quad (11)$$

where δ is the fitting parameter.

Note that σ is temperature dependent which we assume the same as that for $\langle\langle r \rangle\rangle$. The functions $\langle\langle r^n \rangle\rangle$ will be determined below. Note that the vapor phase contacting with the liquid one is the gas of dipole molecules. The van der Waals EOS is appropriate approximation for EOS for such vapor phase. Thus we can get the the critical parameters of this system using the van der Waals theory of the critical point.

The equation (7) leads to the following equations for the critical temperature and density (note that $n_d = n/2$, where n is the total number density):

$$T_c^* = \frac{2\sqrt{2}}{9\sigma^3} \langle\langle r_d^2 \rangle\rangle, \quad \rho_c^* = \frac{1}{\pi\sigma^3}, \quad (12)$$

The estimates for these parameters are straightforward if we put $\sigma = 2$, and take into account that due to small dipole moment of NaCl $\langle\langle r_d^2 \rangle\rangle = 1$ (in units of a):

$$T_c^* = \frac{\sqrt{2}}{36} \approx 0.04, \quad \rho_c^* = \frac{1}{8\pi} \approx 0.04, \quad P_c^* = \frac{\sqrt{2}}{1536\pi} \approx 3 \cdot 10^{-4} \quad (13)$$

$$Z_c = \frac{P_c^*}{\rho_c^* T_c^*} = \frac{3}{16} \approx 0.19$$

which are in satisfactory agreement with the values

$$T_c^* = 0.055, \quad \rho_c^* = 0.026 \quad P_c^* = 3.6 \cdot 10^{-4}, \quad (14)$$

$$Z_c = 0.25$$

obtained within extended Debye-Hückel-Bjerrum theory [6] augmented with ion-dipole interaction. Our value of the critical density is greater due to the neglecting the dissociation of the dipole pairs.

Now we need to consider the dipole pair as itself since the parameters of the potential (6) actually are the averages over the internal partition function of a pair and therefore are the temperature dependent functions.

II. THE DISSOCIATION OF THE ROTATING DIPOLE LIQUID

In previous section the model of undissociated ionic liquid consisting of rotating dipoles has been introduced. Here we investigate the internal structure of the bound pair of ions. We take into account the fact that the energy of interaction of a pair should include centrifugal energy together with Coulombic potential as in standard problem of two bodies interacting via central field.

The dissociation temperature for NaCl-molten is determined by the effective potential of an ion within a rotating dipole which includes the centrifugal energy:

$$kT_d \approx -U_{eff} = \frac{q^2}{r} - \frac{L^2}{2I}, \quad (15)$$

where $I = \mu r^2$ is the moment of inertia of the charge with reduced mass $\mu = \frac{m_+ m_-}{m_+ + m_-} = m/2$. At such high temperatures all degrees of freedom are all in equilibrium and we can use the estimate

$$E_{rot} = \left\langle \frac{L^2}{2I} \right\rangle = kT. \quad (16)$$

Note that the equilibrium distance between ions in a pair, which is determined by the minimum of effective potential (15) with the help of (16), is

$$a_{eq} = \frac{1}{2T^*}, \quad (17)$$

which is exactly the Bjerrum size of the pair R^{Bj} [3] (see also [6]). The choice of (17) as the size of the ionic pair is inappropriate from the physical point of view at low temperatures $T^* \ll 1$ [6]. It is natural that with lowering T the size of a pair should become smaller tending to a at $T \rightarrow 0$. That is why it was suggested to use it for $1/T^* \geq 2$ only.

Let us consider this question within the picture formulated above. To be more correct we will include the rotational energy into association constant, which is proportional to the internal partition function of the pair [6, 8]:

$$K(T^*, R) = 4\pi \int_a^R \exp(-\beta U_{eff}) r^2 dr \quad (18)$$

In 2D case one can put $R = \infty$ because of the logarithmic growth of the electrostatic potential and get the estimation of Kosterlitz-Thouless temperature of dissociation [14]. In 3D case there is the problem with upper cutoff in such an approach where the association constant is identified with internal partition function of the ionic pair.

To define the size of a pair following Bjerrum we investigate the extremal points of the integrand in (18). Doing so we get two solutions:

$$R_-(T^*) = \frac{1 - \sqrt{1 - 16T^*\lambda}}{4T^*}, \quad R_+(T^*) = \frac{1 + \sqrt{1 - 16T^*\lambda}}{4T^*} \quad (19)$$

where

$$\lambda = \frac{L^2/2I_0}{q^2/a}, \quad I_0 = \mu a^2.$$

Here R_+ is solution of the Bjerrum type (minimum of the integrand in (18)), which as has been said above is inappropriate. R_- is another solution corresponding to the maximum of the integrand, which has quite reasonable values and correct behavior at low T^* . It is easy to check that asymptotically for low values of the temperature T^* the value of $K(T^*)$ is formed mainly by the maximum of the integrand. In addition the appropriate limiting behavior to the hard-core contact at formal limit $T^* \rightarrow 0$ is hold provided that $\lambda = 1/2$. This value of λ is in full accordance with the virial theorem [15]. All these facts confirms that we can treat the quantity R_- as the size of the pair even at "high" temperatures $T^* \leq 0.1$. In addition R_- never exceeds 2, i.e. the interparticle the distance when the influence of other pairs and charges on the effective potential can be neglected (see Fig. 1). So we put R_- as the physical cutoff for (18). The existence of such length scale was noted in [6] basing on the the numerical analysis of the function $K(T^*, R)/K(T^*, R^{Bj})$, though only Coulomb potential was included in Boltzmann factor. It gives the rate at which $K(T^*, R)$ rises very rapidly to its plateau value. In our case we find the same behavior of $K(T^*, R)$ at small temperatures, $T^* < 0.04$ (see Fig. 2). Finally we see that there is the natural temperature interval for dipole fluid which is bounded from above by the temperature

$$T_{upper}^* \leq \frac{1}{8} \quad (20)$$

Therefore for $T < T_{upper}^*$ the dipole is stable as itself. Note that the existence of the temperature (20) reminds Kosterlitz-Thouless transition in 2D case. In particular, the centrifugal energy introduced above plays the role analogous to the chemical potential "... required to create a pair of particles of equal and opposite charge at a distance r_0 apart ..." in Kosterlitz-Thouless model [14]. However, in contrast to 2D case in 3D case there is no any divergence in the size of the pair and therefore in its polarizability, but its derivative on the temperature has singular behavior. In other words the temperature derivative of the polarizability is singular but not the polarizability itself. This inference might seem as mere an artifact of introducing the upper cut off in (18). But it should be noted that taking dielectric permittivity ϵ as the order parameter, which is directly connected with polarizability, we get exactly

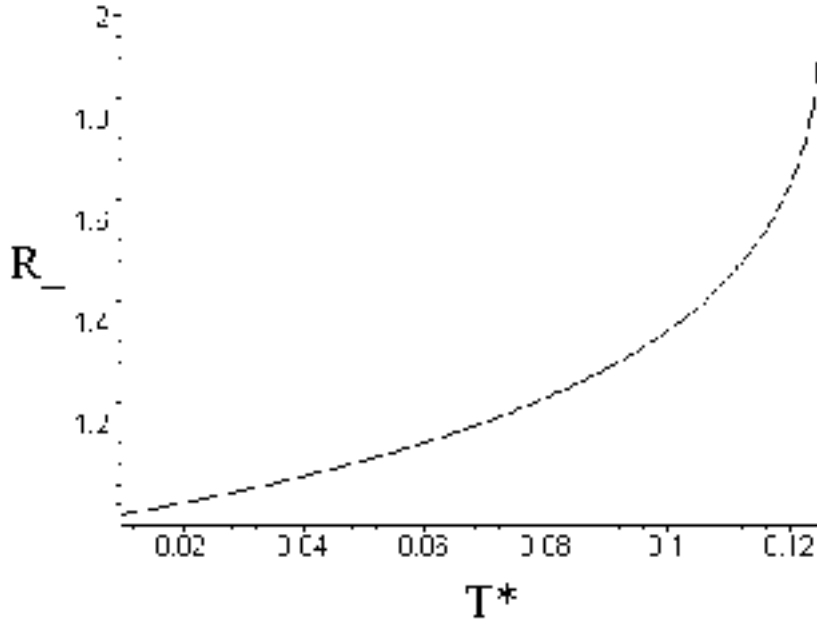


FIG. 1: The temperature dependence of R_- .

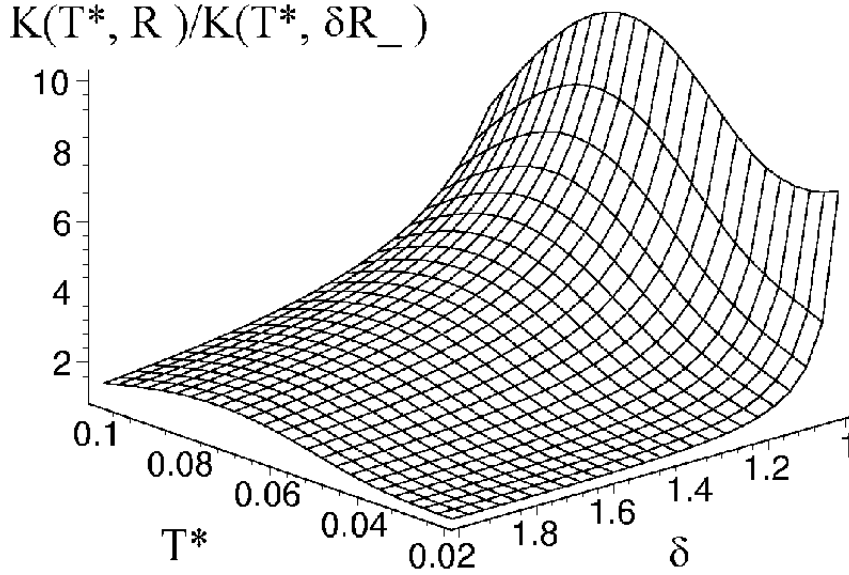


FIG. 2: The ratio $K(T^*, R_+)/K(T^*, \delta \cdot R_-)$ as a function of δ and T^* .

the divergence of its temperature derivative even in mean field approximation. This may serve as additional support for the conjecture of intensive breaking of the dipole pairs at the critical point observed in some numerical experiments [10].

The existence of the interaction between dipoles and the free charges provides additional instability mechanism for their dissociation thus reducing the temperature of "ideal" dissociation (20) because of the polarization of the dipole in the external field of dipole-dipole potential (6) and Coulombic field of free charges. The consideration given above states that there are two characteristic transition in the dipole-dipole fluid: 1) "dipole liquid - dipole gas" critical point of van der Waals type; 2) the smeared dissociation "transition" from associated state to almost completely dissociated one. This smeared transition can be characterized by the temperature on the binodal at which the degree

of dissociation is $1/2$.

The interaction between translational degrees of freedom of the ions is characterized by the critical temperature of the liquid-gas transition, while internal, rotational degrees of freedom are involved into dissociation of such dipole fluid. These degrees of freedom will strongly interact if the corresponding potentials will be of the same magnitude i.e. $T_c \approx T_d$. The additional confirmation of coincidence of such transitions is the high degree of dissociation above the critical point observed in numerical experiments [10, 16] and theoretical models [8], which incorporate dielectric permittivity resulting from the existence of the dipole pairs. This means that T_d cannot be less than T_c . All said above means that in such situation we can not rely on (7) since appropriate EOS should incorporate all relevant interactions which lead to phase separation. In particular the critical temperature is sensitive to the temperature dependence of the parameter $A(T)$.

The condition for the dissociation of a pair in external electrostatic field is:

$$\langle \mathbf{d} \cdot \mathbf{E} \rangle = - \langle \langle U_{eff} \rangle \rangle, \quad (21)$$

where

$$\mathbf{d} = \mathbf{d}_0 + \mathbf{d}_{ind} \quad (22)$$

is the dipole moment, which consists of proper and induced dipole moments. Obviously,

$$\langle \mathbf{d}_0 \cdot \mathbf{E} \rangle = 0, \quad \langle \mathbf{d}_{ind} \cdot \mathbf{E} \rangle = \chi \langle \mathbf{E}^2 \rangle \quad (23)$$

Here χ is the polarizability of a pair. The averaging over the thermal equilibrium gives:

$$\langle \mathbf{E}^2 \rangle = \frac{3k_B T}{\varkappa V_{ph}}, \quad (24)$$

where \varkappa is the dielectric susceptibility of the medium and V_{ph} is the characteristic volume. It is connected with the polarizability of the cavity. According to the definition:

$$\varkappa = \frac{\epsilon - 1}{4\pi} = \frac{1}{2} \chi \rho^* \quad (25)$$

So we get the equation for the temperature in dimensionless form:

$$\frac{6}{\rho^* V_{ph}} T^* = - \langle \langle U_{eff} \rangle \rangle \quad (26)$$

Within the proposed approach we put $V_{ph} = \frac{4\pi}{3} l_c^3$ where l_c is the radius of first coordination sphere. This is the minimal volume for which the conception of continuity of the medium can be applied. By the order of magnitude $l_c \approx 1.5a$. The solution of (26) gives the dependence $T^*(\delta)$. In order to fix the value of δ in the critical point which determine the size of the pair we should equate $T^*(\delta)$ and $T_c^*(\delta)$ obtained above. This way we get:

$$T_c^* = 0.048, \quad \rho_c^* = 0.054, \quad P_c^* = 4.8 \cdot 10^{-4}, \quad \sigma = 1.8, \quad Z_c = 0.19, \quad (27)$$

which are close to those obtained above (13). In notations of [6], $\sigma = 2a_2$. In this work the estimate for the parameter a_2 from simple geometric considerations was given: $0.825 \leq a_2 \leq 1.565$. Thus our estimate is in this interval. From the results obtained above we can infer that the dipole fluid of rotating dipoles in the vicinity of its liquid-gas critical point is about to dissociate. Sure our consideration is incomplete since it does not take into account the existence of free charges.

Finally we estimate the Ginzburg number by the formula used for the molecular liquids [15]:

$$Gi = \left(\frac{r_0}{\xi_0} \right)^6 \quad (28)$$

where $r_0 = \langle \langle r \rangle \rangle \approx a$ is the interparticle spacing within ionic pair and ξ_0 is the amplitude of the correlation length for density fluctuations. Since the density fluctuations are connected with the ones for dipole pairs we put it to be equal $\xi \geq \sigma$. Using the parameters of the critical point found in (27) we get the estimate:

$$Gi \leq 0.04 \quad (29)$$

Discussion

The ionic and dipole liquids form two natural approximations to describe the critical properties of the systems similar the molten NaCl. In our paper we have estimated the main critical parameters for liquid with hard dipole as well as consider the influence of the effects arising due to softness of a dipole molecule. In particular the last is very important to describe the dielectric properties of a system near the critical point. Besides, the variation of molecule parameters due to the rotations allows us to determine the equilibrium size of a ionic pair.

It is not excluded that the quantum corrections to internal states of the dipole pairs will also slightly change the estimates. In particular the temperature dependence of the vibrational contributions to the heat capacity can also be studied. The following step is to construct the equation of state for small "soft" dipole molecules and to take into account the dissociation process with the help of perturbation theory. The combination of such an approach with that developed in [17] on the basis of ionic liquid allows to narrow the region of the most probable values for the critical parameters.

Our estimate for the critical temperature correlates with the known analytical results. Note that most of the analytical approaches based on EOS for low density Coulombic system (DH, MSA etc.) where the dissociation is taken into account perturbatively.

Within the dipole liquid approach we have obtained the estimate for the Ginzburg temperature and have shown that it less than one for the simple liquid by a factor $10^{-2} - 10^{-1}$. The approximation of the dipole liquid allows us to analyze in the evident form the contribution of the polarizational effects [17]. One can show that the lasts lead to the further considerable decrease of the Ginzburg temperature.

Note also the possibility for the appearance of new inhomogeneous phase near the critical point of ionic liquids. Since the dissociation temperature T_d is near T_c , the system can desintegrate on the regions with the essentially different values of the ionization degree Δ : the drops of ionic and dipole liquids. As a consequence the region with the Ising-like behavior cannot be reached. This scenario needs in very careful investigation. These and other questions will be the subjects of further works.

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